

Relativistic separable dual-space Gaussian Pseudopotentials from H to Rn

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We generalize the concept of separable dual-space Gaussian pseudopotentials to the relativistic case. This allows us to construct this type of pseudopotential for the whole periodic table and we present a complete table of pseudopotential parameters for all the elements from H to Rn. The relativistic version of this pseudopotential retains all the advantages of its nonrelativistic version. It is separable by construction, it is optimal for integration on a real space grid, it is highly accurate and due to its analytic form it can be specified by a very small number of parameters. The accuracy of the pseudopotential is illustrated by an extensive series of molecular calculations.

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I. INTRODUCTION

Pseudopotentials are a well established tool in *ab initio* structure calculations of molecules and solids. First, by replacing the atom by a pseudo atom the number of orbitals which have to be calculated is reduced and second, the size of the basis set can substantially be reduced because the pseudo wave functions are smoother than their all-electron counterparts. In addition relativistic effects which are relevant for heavier elements can be included in the pseudopotential construction so that a non-relativistic calculation can reproduce these

In 1982 Bachelet, Hamann and Schlüter¹ published a list of pseudopotentials for all elements up to Pu, that has found widespread application. There have been many attempts to improve the pseudopotential transferability and their numerical efficiency since. One major advance was the introduction of a separable form by Kleinmann and Bylander², that significantly reduces the computational effort for the calculation of the nonlocal part especially when using a plane wave basis set. Gonze, Stumpf and Scheffler³ investigated the Kleinmann-Bylander form carefully and published a list⁴ of pseudopotentials for many elements up to Xe. Goedecker *et al.*⁵ proposed a new dual-space Gaussian type pseudopotential which is separable and satisfies an optimality criterion for the real space integration of the nonlocal part. For large systems there is only a quadratic scaling with respect to the system size if the integration of the nonlocal part is performed on a real space grid compared to a cubic scaling if a Fourier space integration is used⁶. In contrast to most other pseudopotential construction methods Goedecker *et al.* also included unoccupied orbitals

in their method thereby generating highly transferable pseudopotentials. Goedecker *et al.* gave the non relativistic pseudopotential parameters for the first two rows of the periodic system and showed that their pseudopotentials give highly accurate results in molecular calculations. They obtained results which are much closer to the quasi-exact all-electron LDA^{11,12} (local density approximation) value than what is obtained in all-electron calculations with a standard Gaussian 6-31G* basis sets. With other words the errors due to the pseudopotential approximation were much smaller than the errors in a all-electron calculation introduced by incomplete basis sets.

In this paper we give the parameters of dual-space Gaussian pseudopotentials for all elements from H to Rn. In contrast to Goedecker *et al.* all pseudopotentials are now generated on the basis of a fully relativistic all-electron calculation, i.e. by solving the two component Dirac equation. The generalization of the norm-conservation property to the relativistic case proposed by Bachelet and Schlüter¹⁶ is used for the construction. We also introduced some slight modifications of the analytic form of the pseudopotential. The parameters are given in the context of the local density approximation. Even though the parameters change only slightly if the pseudopotential is constructed within the framework of a generalized gradient approximation^{14,15} (GGA) functional, we found that molecular properties are less accurately described if LDA pseudopotentials are inserted in a molecular calculation using GGA's. Since it is not possible to construct pseudopotentials tables for all current GGA schemes, a program that can construct pseudopotentials for the most common GGAs can be obtained from the authors.

II. FORM OF THE PSEUDOPOTENTIAL

The local part of the pseudopotential is given by

$$V_{\text{loc}}(r) = \frac{-Z_{\text{ion}}}{r} \text{erf}\left(\frac{r}{\sqrt{2}r_{\text{loc}}}\right) + \exp\left[-\frac{1}{2}\left(\frac{r}{r_{\text{loc}}}\right)^2\right] \times \left[C_1 + C_2\left(\frac{r}{r_{\text{loc}}}\right)^2 + C_3\left(\frac{r}{r_{\text{loc}}}\right)^4 + C_4\left(\frac{r}{r_{\text{loc}}}\right)^6\right] \quad (1)$$

where erf denotes the error function. Z_{ion} is the ionic charge of the atomic core, i.e. the total charge minus the charge of the valence electrons. The nonlocal contribution $V_l(\mathbf{r}, \mathbf{r}')$ to the pseudopotential is a sum of separable terms

$$V_l(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^3 \sum_{j=1}^3 \sum_{m=-l}^{+l} Y_{l,m}(\hat{\mathbf{r}}) p_i^l(r) h_{i,j}^l p_j^l(r') Y_{l,m}^*(\hat{\mathbf{r}}') \quad (2)$$

where $Y_{l,m}$ are the spherical harmonics and l the angular momentum quantum number. The projectors $p_i^l(r)$ are Gaussians of the form

$$p_i^l(r) = \frac{\sqrt{2} r^{l+2(i-1)} \exp\left(-\frac{r^2}{2r_i^2}\right)}{r_i^{l+(4i-1)/2} \sqrt{\Gamma(l + \frac{4i-1}{2})}} \quad (3)$$

where Γ denotes the gamma function. The projectors satisfy the normalisation condition

$$\int_0^\infty p_i^l(r) p_i^l(r) r^2 dr = 1. \quad (4)$$

It is a special property of our pseudopotential that it has also an analytical form if expressed in reciprocal space. The Fourier transform of the pseudopotential is given by

$$\begin{aligned} V_{\text{loc}}(g) = & -\frac{4\pi Z_{\text{ion}}}{\Omega g^2} e^{-\frac{(gr_{\text{loc}})^2}{2}} \\ & + \sqrt{8\pi^3} \frac{r_{\text{loc}}^3}{\Omega} e^{-\frac{(gr_{\text{loc}})^2}{2}} \times \{C_1 + C_2 (3 - g^2 r_{\text{loc}}^2) \\ & + C_3 (15 - 10(gr_{\text{loc}})^2 + (gr_{\text{loc}})^4) + C_4 (105 \\ & - 105(gr_{\text{loc}})^2 + 21(gr_{\text{loc}})^4 - (gr_{\text{loc}})^6)\} \end{aligned} \quad (5)$$

for the local part and

$$\begin{aligned} V_l(\mathbf{g}, \mathbf{g}') = & (-1)^l \sum_{i=1}^3 \sum_{j=1}^3 \sum_{m=-l}^{+l} Y_{l,m}(\hat{\mathbf{g}}) p_i^l(g) \\ & \times h_{i,j}^l p_j^l(g') Y_{l,m}^*(\hat{\mathbf{g}}') \end{aligned} \quad (6)$$

for the nonlocal part. The Fourier transform of the projectors $p_i^l(r)$ can be calculated analytically and for the relevant cases one obtains

$$p_1^{l=0}(g) = \frac{4\sqrt{2r_0^3}\pi^{5/4}}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_0)^2]}, \quad (7)$$

$$p_2^{l=0}(g) = \frac{8\sqrt{\frac{2r_0^3}{15}}\pi^{5/4}(3 - g^2 r_0^2)}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_0)^2]}, \quad (8)$$

$$p_3^{l=0}(g) = \frac{16\sqrt{\frac{2r_0^3}{105}}\pi^{5/4}(15 - 10g^2 r_0^2 + g^4 r_0^4)}{3\sqrt{\Omega} \exp[\frac{1}{2}(gr_0)^2]}, \quad (9)$$

$$p_1^{l=1}(g) = \frac{8\sqrt{\frac{r_1^5}{3}}\pi^{5/4}g}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_1)^2]}, \quad (10)$$

$$p_2^{l=1}(g) = \frac{16\sqrt{\frac{r_1^5}{105}}\pi^{5/4}g(5 - g^2 r_1^2)}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_1)^2]}, \quad (11)$$

$$p_3^{l=1}(g) = \frac{32\sqrt{\frac{r_1^5}{1155}}\pi^{5/4}g(35 - 14g^2 r_1^2 + g^4 r_1^4)}{3\sqrt{\Omega} \exp[\frac{1}{2}(gr_1)^2]}, \quad (12)$$

$$p_1^{l=2}(g) = \frac{8\sqrt{\frac{2r_2^7}{15}}\pi^{5/4}g^2}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_2)^2]}, \quad (13)$$

$$p_2^{l=2}(g) = \frac{16\sqrt{\frac{2r_2^7}{105}}\pi^{5/4}g^2(7 - g^2 r_2^2)}{3\sqrt{\Omega} \exp[\frac{1}{2}(gr_2)^2]}, \quad (14)$$

$$p_1^{l=3}(g) = \frac{16\sqrt{\frac{r_3^9}{105}}\pi^{5/4}g^3}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_3)^2]}. \quad (15)$$

In both real and Fourier space the projectors have the form of a Gaussian multiplied by a polynomial. Due to this property the dual-space Gaussian pseudopotential is the optimal compromise between good convergence properties in real and Fourier space. The multiplication of the wave function with the nonlocal pseudopotential arising from an atom can be limited to a small region around the atom as the radial projectors $p_i^l(r)$ asymptotically tend to zero outside the covalent radius of the atom. In addition, a very dense integration grid is not required as the nonlocal pseudopotential is reasonably smooth because of its good decay properties in Fourier space.

The use of this form for the pseudopotential is also very advantageous if atom centered basis functions are used instead of plane waves. Because of the separability all three-center integrals are products of two-center integrals and so only these two-center integrals have to be calculated. If atom centered Gaussian type orbitals are used, these two-center integrals can easily be evaluated analytically.

In the relativistic case the spin orbit coupling splits up all orbitals with $l > 0$ into a spin up and spin down orbital with overall angular momentum $j = l \pm 1/2$. So for each angular-momentum $l > 0$ one spin up and spin down orbital with different wave functions and pseudopotentials exist. Following Bachelet and Schlüter¹⁶ we give a weighted average and difference potential of these potentials. The average pseudopotential is conveniently defined as

$$V_l(\mathbf{r}, \mathbf{r}') = \frac{1}{2l+1} (lV_{l-1/2}(\mathbf{r}, \mathbf{r}') + (l+1)V_{l+1/2}(\mathbf{r}, \mathbf{r}')) \quad (16)$$

weighted by the different j degeneracies of the $l \pm 1/2$ orbitals. The difference potential describes the spin orbit coupling and is defined as

$$\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}') = \frac{2}{2l+1} (V_{l+1/2}(\mathbf{r}, \mathbf{r}') - V_{l-1/2}(\mathbf{r}, \mathbf{r}')). \quad (17)$$

The total pseudopotential is then given by

$$V(\mathbf{r}, \mathbf{r}') = V_{\text{loc}}(r)\delta(\mathbf{r} - \mathbf{r}') + \sum_l V_l(\mathbf{r}, \mathbf{r}') + \Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}') \mathbf{L} \cdot \mathbf{S}. \quad (18)$$

where $V_{\text{loc}}(r)$ and $V_l(\mathbf{r}, \mathbf{r}')$ are now scalar relativistic quantities but with the same form (eq.(1,2)) as the non relativistic case. To express $\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}')$ we also use eq.(2) just replacing the $h_{i,j}^l$ by different parameters $k_{i,j}^l$, i.e.

$$\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^3 \sum_{j=1}^3 \sum_{m=-l}^{+l} Y_{l,m}(\hat{\mathbf{r}}) p_i^l(r) k_{i,j}^l p_j^l(r') Y_{l,m}^*(\hat{\mathbf{r}}'). \quad (19)$$

Neglecting the contributions from $\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}')$ in eq.(18) gives the average potential that contains all scalar parts of the relativistic pseudopotential whereas the total potential contains relativistic effects up to order α^2 .

III. DETERMINATION OF THE PSEUDOPOTENTIAL PARAMETERS

The parameters of the pseudopotentials were found by minimising the differences between the eigenvalues and the charges within an atomic sphere of the all-electron and the pseudo atom. In most cases the radius of the atomic sphere was taken to be the covalent radius of the atom. For consistency we always performed a fully relativistic calculation for the all-electron atom even when relativistic effects are negligible. The exchange and correlation energy was calculated with the functional given by Goedecker *et al.*⁵ This functional reproduces very well the Perdew-Wang¹⁷ 1992 but is much easier to compute. To ensure transferability of the pseudopotential we also considered the next two or three higher unoccupied orbitals for each angular-momentum and the lowest orbital of the next two unoccupied angular-momentum. However in our calculations we never exceeded $l_{\text{max}}=3$. The atom was put in an external parabolic confining potential to have well defined unoccupied orbitals. The pseudopotential parameters given in table I typically reproduce the eigenvalues of the occupied orbitals with an error of less than 10^{-5} a.u. and for the unoccupied orbitals to within 10^{-3} a.u. Pseudopotentials containing semi-core electrons (next Sec.) are an exception as the errors for the semi-core orbitals are usually larger than for the valence orbitals. In many cases we found it unnecessary to include all unoccupied orbitals in our fitting procedure. For most cases the inclusion of only the first unoccupied orbital for an angular-momentum results in comparable good results for the following higher unoccupied orbitals. Nevertheless we always checked all-electron and pseudo eigenvalues and charges of the unoccupied orbitals to verify this.

It has already been discussed by Goedecker *et al.* that our fitting procedure yields pseudopotentials that obey

the norm-conservation⁷ condition and meet several additional conditions⁸⁻¹⁰, such as extended norm conservation and hardness, thereby leading to pseudopotentials of a very high quality.

In table III we give the transferability errors for several excited and ionized states for some elements.

The construction of our pseudopotential differs somehow from the usual method because we fit the pseudopotential parameters that give the best overall representation for the eigenvalues and charges of several orbitals rather than producing pseudo wave functions that are identical to their all-electron counterparts beyond some cutoff radius. Therefore the wave functions of the pseudo atom and all-electron atom approach each other only exponentially. Nevertheless the difference is very small beyond the core region as can be seen from Fig. 1. A second consequence of our fitting procedure is that contrary to most other pseudopotential construction methods the local part of our pseudopotential does not correspond to a certain wave function.

It is as special feature of our method that we fit our parameters directly against the all-electron eigenvalues and charges rather than fitting analytical or numerical potentials that reproduce pseudo wave functions which themselves are constructed from their all-electron counterparts. Therefore our pseudopotentials require significant fewer parameters than those tabulated by Bachelet, Hamann and Schlüter¹. During the generation of our pseudopotentials we found that there is in general no single minimal parameter set that gives the best overall pseudopotential for one atom. This finding is different to the former study of Goedecker *et al.* where only the first two rows of the periodic table have been considered. We always tried to use the minimum parameter set which is sufficient to reproduce the desired accuracy of the fitted eigenvalues and charges. Identical parameter sets were used for comparable elements, i.e. the same parameter set was used for all 3d-elements or the 4d-elements, respectively. The fitting of the pseudopotential parameters is numerically demanding as many local minima exist so that sometimes up to some 10^5 pseudopotential evaluations are necessary until one finds good parameter values. We used a slow Simplex-Downhill algorithm¹⁸ for the optimisation that proved to be much more robust than more sophisticated methods. The pseudopotential parameter r_{loc} was set by hand except for the first row because this parameter is not easy accessible by our fitting procedure. For many elements we generated and tested pseudopotentials with different values of r_{loc} . After selection of the optimum pseudopotentials the r_{loc} values for the elements in between were interpolated so that no discontinuities occur.

IV. SEMI-CORE ELECTRONS

For many atoms there is no unambiguous separation of the electronic system into a well isolated core and valence shell. For example it is well known the $(n-1)$ p -levels of the heavy alkali atoms are relatively shallow in energy and extended in space. The $3d$ -wave functions of the $3d$ -elements are strongly localized so that there is a significant overlap with the $3(s, p)$ -wave functions although the later are much lower in energy than the $3d$ - and $4(s, p)$ -valence wave functions. The same is true for the $4d$ - and $5d$ -elements. Analogous the $4f$ -wave functions of the $4f$ -elements are so localized that they overlap with the $5s$ - and $5p$ -wave functions. In all these cases where a non negligible overlap between valence and core wave functions exists the frozen-core approximation underlying the construction of all pseudopotentials is not well satisfied. One way to overcome this problem is the inclusion of a nonlinear core correction¹⁹ that considers the contribution of the core charge to the exchange-correlation potential. The other more straight forward solution is the explicit inclusion of the semi-core electrons into the pseudopotential. In this work we decided for the second method. This ensures that our semi-core pseudopotentials still can be used with programs where non linear corrections are not considered. In addition the explicit inclusion of the semi-core electrons ensures that our pseudopotentials still work well for systems where non linear core corrections fail. It is unnecessary that the eigenvalues and charge distribution of the semi-core wave functions have the same accuracy as the valence wave functions of the pseudo atom. We always tried to generate semi-core pseudopotentials with semi-core pseudo wave functions that are as smooth as possible but still yield accurate results for the valence wave functions. Therefore the error for the eigenvalues of semi-core wave functions for our pseudopotentials is within 10^{-3} to 10^{-2} a.u. which is about 3 orders of magnitude worse than the typically error for the valence wave functions.

The choice which electrons are treated as semi-core electrons also depends on the required accuracy. As we were interested to generate pseudopotentials that can be used together with plane wave basis sets within a reasonable computational effort we tried to include not too many semi-core electrons into our pseudopotentials. Our semi-core pseudopotentials for the group Ia and IIa elements, the transition metals of group IIb to VIIIb and the lanthanides treat the $(n-1)s$ - and the $(n-1)p$ -electrons as semi-core electrons. For the elements of group Ib, IIb and IIIa (except B and Al) all electrons of the completely filled nd -shell are treated as semi-core electrons.

For all elements mentioned above semi-core wave functions improve the description of highly positive charged ions. In table III the transferability error of two Ti pseudopotentials is listed for several states. For most states the calculated excitation energies are much closer to the all-electron values for the Ti semi-core pseudopotential

including the $3s$ - and $3p$ -semi-core electrons. This is most significant for the $4s^0 4p^0 3d^0$ state which corresponds to a Ti^{4+} -ion. For the $4e$ -pseudopotential the error is 0.1 Hartree but only 0.28×10^{-2} Hartree for the $12e$ -semi-core pseudopotential.

Pseudopotentials with semi-core wave functions always require higher computational effort. They contain more electrons and larger basis sets are necessary for a sufficient description of the localized semi-core wave functions. In many applications like molecular structure calculation semi-core pseudopotentials yield converged results with comparable small basis sets even if the calculated total energy is still far from its converged value. Therefore the inclusion of semi-core electrons not inevitably requires the use of extremely large basis sets. In fact in our molecular calculations the highest plane wave energy cutoff were needed for calculations with the fluorine pseudopotential which has no semi-core electrons at all.

In many cases it is not quite clear, if semi-core electrons play an important role or not. For most applications the need to use semi-core pseudopotentials depends on the required accuracy and necessary computational effort and should be tested carefully. Therefore we constructed both type of pseudopotentials for most elements where semi-core electrons can play a significant role in electronic structure calculations.

V. MOLECULES

We tested our pseudopotentials by calculating the bond lengths of a large number of molecules. In all calculations we used our scalar relativistic pseudopotentials neglecting the terms for spin orbit interaction. Whenever possible we tried to determine values for the bond lengths, that are converged to $\approx 10^{-3}$ Bohr. To obtain this high level of accuracy extremely large boxes and high plane wave energy cutoffs were needed so that for some molecules the accuracy of the calculations was limited by our computational resources. The calculated bond lengths together with their experimental values are listed in table II. As a reference for the quasi-exact LDA value we also list the bond lengths calculated with GAUSSIAN 94²⁰ using a 6-311G++(3df,3pd) basis set (for the $3d$ -elements no f -polarization functions have been used). With a few exceptions the values calculated with GAUSSIAN 94 agree within a few thousands of a Bohr with the LDA results published by Dickson and Becke²¹ and therefore should be close to the LDA limit. For some molecules where no high precision basis sets are available we took the all-electron results from Dickson and Becke. To estimate the error arising from the pseudopotential approximation our calculated values should be compared with these LDA results rather than with the experimental bond lengths. Unfortunately exact LDA values for molecules containing heavier elements often are not avail-

able because of the lack of a sufficiently accurate basis set.

The bond lengths calculated with our pseudopotentials, including semi-core electrons where necessary, agree very well with the all-electron values obtained with GAUSSIAN 94. The error of the pseudopotential approximation for first row atoms is nearly ten times smaller than the LDA error and for the heavier elements at least comparable to the LDA error. In all cases except for the non semi-core pseudopotentials the accuracy relative to the exact LDA value is, however, better than the results obtained with standard Gaussian 6-31G* basis sets and it is comparable or better than the results obtained with other all-electron methods. It must be mentioned that our results especially for molecules with heavier elements are not exactly comparable to the values obtained with GAUSSIAN 94 or the values of Dickson and Becke as our pseudopotentials also include relativistic effects.

For some non semi-core pseudopotentials the error in the calculated bond lengths is quite large. Nevertheless these pseudopotentials may still be of interest for electronic structure calculations if no high precision is required or the computational resources are limited. These pseudopotentials require only small basis sets which is sometimes a necessity for the study of large systems.

Our calculated bond lengths containing only first or second row atoms also agree to within one or two thousands of a Bohr to those obtained with nonrelativistic versions of these pseudopotentials that have already been published⁵ (differences in the case of HCN are due to the choice of a different simulation box). This clearly demonstrates that relativistic effects do not influence the bond lengths for these molecules on a relevant scale.

VI. THE PARAMETERS

In the following we list the parameters for all elements up to Rn. The entries in Table I have the following meaning:

Element	Z_{ion}	r_{loc}	C_1	C_2	C_3	C_4
		r_0	$h_{1,1}^0$	$h_{2,2}^0$	$h_{3,3}^0$	
		r_1	$h_{1,1}^1$	$h_{2,2}^1$	$h_{3,3}^1$	
			$k_{1,1}^1$	$k_{2,2}^1$	$k_{3,3}^1$	
		r_2	$h_{1,1}^2$	$h_{2,2}^2$	$h_{3,3}^2$	
			$k_{1,1}^2$	$k_{2,2}^2$	$k_{3,3}^2$	
		\vdots				

Only the nonzero parameters are shown in table I. Parameters for elements marked with ^{sc} correspond to semi-core pseudopotentials. In order to keep the table as small as possible the coefficients $h_{i,j}^l$ and $k_{i,j}^l$ of the nonlocal projectors for $i \neq j$ are not listed. To get the full parameter set the missing $h_{i,j}^l$ and $k_{i,j}^l$ have to be calculated from the $h_{i,i}^l$ and $k_{i,i}^l$. The relevant equations for the $h_{i,j}^l$ are:

$$h_{1,2}^0 = -\frac{1}{2}\sqrt{\frac{3}{5}}h_{2,2}^0, \quad (20)$$

$$h_{1,3}^0 = \frac{1}{2}\sqrt{\frac{5}{21}}h_{3,3}^0, \quad (21)$$

$$h_{2,3}^0 = -\frac{1}{2}\sqrt{\frac{100}{63}}h_{3,3}^0, \quad (22)$$

$$h_{1,2}^1 = -\frac{1}{2}\sqrt{\frac{5}{7}}h_{2,2}^1, \quad (23)$$

$$h_{1,3}^1 = \frac{1}{6}\sqrt{\frac{35}{11}}h_{3,3}^1, \quad (24)$$

$$h_{2,3}^1 = -\frac{1}{6}\sqrt{\frac{14}{11}}h_{3,3}^1, \quad (25)$$

$$h_{1,2}^2 = -\frac{1}{2}\sqrt{\frac{7}{9}}h_{2,2}^2, \quad (26)$$

$$h_{1,3}^2 = \frac{1}{2}\sqrt{\frac{63}{143}}h_{3,3}^2, \quad (27)$$

$$h_{2,3}^2 = -\frac{1}{2}\sqrt{\frac{18}{143}}h_{3,3}^2, \quad (28)$$

$$h_{i,j}^l = h_{j,i}^l. \quad (29)$$

By this procedure one obtains a set of projector functions

$$P_k^l(r) = \sum_{i=1}^k \sum_{j=1}^k h_{i,j}^l P_{i,j}^l(r), \quad k = 1, 2, 3 \quad (30)$$

that satisfy the orthogonality relation

$$\int_0^\infty P_i^l(r) P_j^l(r) r^2 dr = 0 \quad \text{for } i \neq j. \quad (31)$$

Replacing $h_{i,j}^l$ by $k_{i,j}^l$ in eq.(20-29) gives the equations for the $k_{i,j}^l$. We found that the orthogonalization of the projectors improves the fitting procedure of our pseudopotential rather than keeping all $h_{i,j}^l$ zero for $i \neq j$ as was done in the former work of Goedecker *et al.*⁵ Treating the $h_{i,j}^l$ as independent pseudopotential parameters does not improve the results.

VII. SUMMARY

We developed a complete set of relativistic LDA pseudopotentials for the whole periodic system up to Rn. The pseudopotentials are easy to use as only a few parameters are necessary. All terms for both Fourier and real space are given analytically and no tabulated functions are needed. The pseudopotentials are highly accurate and transferable and have been tested in extensive atomic and molecular calculations.

Gaussian type pseudopotentials for other exchange correlation functionals or gradient corrected functionals can easily be constructed using our LDA parameter sets as an initial guess. The necessary programs are available from the authors upon request.

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		.334235	6.925740	-3.142005				.259140	11.195226	-7.845825		
		.242416	5.079086	-6.284281				.251425	-.551464	-4.639237		
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		.242947	-9.125896					.221665	-12.075354			
			.005822						.011475			
V	5	.690000						Ni	10	.560000		
		.514704	2.208670	1.896763	3.076377				.425399	3.619651	3.088965	3.058598
		.743504	1.115751	.286649					.584081	1.742220	.386341	
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		.374890	-5.841633						.278113	-11.608428		
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V ^{sc}	13	.375000	4.941291	-.096443				Ni ^{sc}	18	.350000	3.610311	.449638
		.326651	7.659390	-3.892229					.245105	12.161131	-9.078929	
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			.156408	.008030						.269572	-.143442	
		.240792	-8.828518						.214950	-13.395062		
			.006548							.013538		
Cr	6	.660000						Cu	1	.580000		
		.498578	2.400756	2.072337	2.952179				.843283	.975787	-.822070	-.133237
		.719768	1.145557	.278236					1.089543	.024580	-.249001	
			-.013176	.035625						.010792	-.006734	
		.354341	-6.615878						1.291602	-.065292		
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Cr ^{sc}	14	.370000	5.113362	-.646819				Cu ^{sc}	11	.530000		
		.306011	8.617835	-4.137695					.423734	3.888050	3.276584	2.290091
		.241090	3.161588	-5.032906					.572177	1.751272	.374943	
			.169781	.000411						-.024067	.076481	
		.219577	-11.157868						.266143	-12.676957		
			.009007							.010489		
Mn	7	.640000						Zn	2	.570000		
		.481246	2.799031	2.486101	2.565630				.640712	2.088557	-.218270	-.941317
		.669304	1.368776	.316763					.967605	.163546	-.227086	
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		.327763	-7.995418						1.330352	.010486		
			.004536							.000225		
Mn ^{sc}	15	.365000	6.748683	-.576569				Zn ^{sc}	12	.510000		
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		.254536	.371176	-4.229057					.539618	2.023884	.431742	
			.164188	-.039396						-.025759	.090915	
		.221422	-12.115385						.252151	-14.338368		
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Fe	8	.610000						Ga	3	.560000		
		.454482	3.016640	2.583038	3.257635				.610791	2.369325	-.249015	-.551796
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		.308732	-9.145354						.982580	.075437		
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Fe ^{sc}	16	.360000	5.392507	-.030066				Ga ^{sc}	13	.490000		
		.269268	10.193723	-6.834982					.384713	4.831779	4.238168	2.833238
		.247686	.145613	-5.234954					.586130	1.940527	-.299738	
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		.223021	-12.026941						.240803	-15.795675		
			.010322							.015503		
Co	9	.580000						Ge	4	.540000		
		.440457	3.334978	2.873150	3.091028				.493743	3.826891	1.100231	-1.344218
		.610048	1.634005	.356083					.601064	1.362518	-.627370	
			-.017521	.058766						.043981	.009802	
		.291661	-10.358800						.788369	.191205		
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Se	6	.510000				Zr ^{sc}	12	.470000	15.782342	.433648	
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		.472473	2.858806	-.590671				.388558	-.794123	-3.172114	
			.062196	.064907					.301247	-.098654	
		.613420	.434829					.520496	-1.548402	.826127	
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Br	7	.500000				Nb	5	.724000	4.021058		
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		.455323	3.108823	-.632202				.846672	.609675	.596788	
			.074007	.068787					-.080816	.125243	
		.557847	.555903					.516072	-2.696830	-1.694967	
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Kr	8	.500000				Nb ^{sc}	13	.460000	13.505394	.752434	
		.410759	5.911194	1.967372	-1.458069			.393708	3.222025	-4.599342	
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			.087011	.086008					.246821	-.086659	
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Rb	1	1.096207	.847333	-.748120		Mo	6	.699000	7.995868		
		.955699	.887460	.903088	-.006750			.678126	1.289607	.998113	
		1.156681	.461734	.336113				.800771	.301412	.741615	
			-.043443	.057876					-.104124	.153906	
		.664323	-1.362938					.453384	-2.809708	-6.820946	
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Rb ^{sc}	9	.490000	4.504151	-.741018		Mo ^{sc}	14	.430000	16.237452	1.496536	
		.282301	9.536329	9.486634				.376255	3.362426	-5.289276	
		.301886	2.209592	5.475249				.361734	-.379571	-4.067713	
			-.867379	1.237532					.378681	-.124561	
		.514895	.449376					.525828	-1.543211	1.074388	
			.008685						.014460	-.014769	
Sr	2	1.010000	.684749	-.062125		Tc	7	.673000	13.315381		
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		1.174178	.439983	.018267				.784275	.028673	.658363	
			.004022	.022207					-.080760	.140668	
		.743175	-1.386990					.519890	-5.984224	.721822	
			.002846						.026025	-.041776	
Sr ^{sc}	10	.480000	5.571455	-1.079963		Tc ^{sc}	15	.430000	14.910011	1.046381	
		.275441	9.995135	9.336679				.369721	3.917408	-5.268399	
		.302243	3.169126	4.049231				.357772	-.270000	-3.737771	
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Y	3	.900000	-.343891			Ru	8	.647214	8.687723		
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		.949864	.780950	.368739				.746425	.639012	.650376	
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		.653851	-1.256930	-.075368				.440358	-4.883365	-3.063746	
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Y ^{sc}	11	.475000	13.217914	1.353178		Ru ^{sc}	16	.430000	13.582571	.596227	
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Rh ^{sc}	17	.420000	15.225012	.415911			Sb	5	.590000	6.680228	
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			.033797	-.047798						.010809	
Pd ^{sc}	18	.410000	15.720259	.140765			I	7	.560000	14.661825	
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Ag	1	.650000	-2.376061				Xe	8	.560000	12.734280	
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		1.235842	.130081	-.277495					.541024	1.130043	-.752764
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Ag ^{sc}	11	.570000	1.017053				Cs	1	1.200000		
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		.630009	1.813968	1.304450					1.280478	.244893	.227279
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Cd ^{sc}	12	.550000	2.382713						.333507	-17.948259	
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		.377874	-4.190072	-.770156					1.016187	.922593	.763495
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			.058765	-.073414			La ^{sc}	11	.535000	19.909308	-1.474830
									.551775	1.293272	-1.121819
Sn	4	.605000	4.610912						.476308	1.172527	-.828810
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Ce ^{sc}	12	.535000	18.847470	-.765636			.482809	-.625802		
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			.463710	.090257	.012566			.016197		
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		.306717	-17.214790				.434642	.014315	-2.046238	.000000
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Pr ^{sc}	13	.532083	18.424739	-.657669			.467229	-.668924		
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		.458897	1.117060	-1.852109	.000000		.261670	-23.922358		
			.314280	.350982	-.165254			.017938		
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Nd ^{sc}	14	.529167	17.815030	-.594798			.447131	-.742863		
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			-.214396	1.100446	-.832670			.019830		
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			.611413				.419948	2.144503	-3.984203	
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Pm ^{sc}	15	.526250	18.251723	-.492107			.418385	-.999006		
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		.472260	.160512	-1.565305	.000000		.249126	-26.696809		
			-.339955	1.359017	-1.145883			.021783		
		.473709	-.429952			Tm ^{sc} 23	.502917	17.247293	-1.627697	
			.064044				.413373	1.947196	-4.121556	
		.291527	-19.305057				.409923	-.094493	-2.224087	.000000
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Sm ^{sc}	16	.523333	17.206792	-.532803			.392870	-1.353308		
		.479677	1.723635	-2.659367				.119299		
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			-.240300	1.200867	-1.054041			.023833		
		.470840	-.410630			Yb ^{sc} 24	.500000	17.357144	-1.773916	
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			.011924					-.349470	2.074295	-1.814297
Eu ^{sc}	17	.520417	17.373516	-.648468			.444025	-.889967		
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		.445907	.518046	-2.135186	.000000		.238298	-29.932854		
			.252258	.584324	-.480586			.025718		
		.490038	-.426120			Lu ^{sc} 25	.497000	17.037053	-1.661610	
			.051028				.391206	2.184678	-5.432346	
		.278401	-20.946528				.393896	-.719819	-2.723799	.000000
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Gd ^{sc}	18	.517500	17.512556	-.719534			.436518	-1.173245		
		.462014	1.551856	-3.068703				.072130		
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			.053128				.422810	2.564442	-6.013732	1.109760
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		.607504	-.331637	-.121021			.930121	-.379865	-.262716
		.426388	1.459363	-5.282764			.376428	.754315	-5.875580
			.222119	-.121283				.219517	-.112145
Ta	5	.744000	3.623116			Pt	10	.616000	11.027417
		.581801	2.005338	3.027036				.520132	2.447430
		.770646	.518567	1.185378				.658976	.408453
			-.485635	.695148					1.647716
		.534370	-2.202200	-1.666675				.451243	-.763296
			.086716	-.094635					1.065883
Ta ^{sc}	13	.550000	4.546236	.779422		Pt ^{sc}	18	.500000	5.445832
		.421853	2.708136	-5.790959	.947663			.409942	2.994366
		.461345	-.724853	-2.215211	.000000			.398652	-7.448772
			.649992	-.336371	-.101322				-3.776974
		.410994	1.348495	-5.386947					1.017060
			.205344	-.102353				.367964	-.348213
									-5.755431
W	6	.719000	4.058450					.226472	-.114346
		.582463	2.161166	2.741500		Au	1	.650000	-1.963712
		.742307	.600973	1.299943				.919308	-1.698123
			-.509800	.751739				1.140351	1.539599
		.534959	-2.517063	-.789137					-.468779
			.075772	-.086193					-.792039
W ^{sc}	14	.540000	4.800251	.901544				.039349	-.497538
		.418570	2.692204	-6.022637	1.218316				-.209758
		.449555	-.702084	-2.451680	.000000				1.32970
			.715480	-.385339	-.077093				-.153427
		.399602	1.177436	-5.553621		Au ^{sc}	11	.590000	11.604428
			.205860	-.100046				.521180	2.538614
Re	7	.693000	8.180816					.630613	.394853
		.509816	2.269379	3.528529					2.057831
		.745839	.496693	.925829					1.296571
			-.370589	.616765				.440706	-.960055
		.500954	-3.689630	-1.894601					-4.719070
			.111557	-.131595					-1.650429
Re ^{sc}	15	.530000	5.592660	.943957		Hg	2	.640000	-.148484
		.403252	2.760720	-6.396415	.868732				-3.296329
		.440951	-.900546	-2.511211	.000000			.812108	1.765041
			.788715	-.489984	-.017012			1.053714	-.466127
		.390395	.875251	-5.672543					-.531816
			.209737	-.102862					-.092330
Os	8	.667000	9.440459					1.100000	.120638
		.510307	2.402367	3.046706					.020931
		.717553	.499523	1.053284		Hg ^{sc}	12	.570000	2.134572
			-.430746	.701752				.521802	3.293920
		.487586	-4.142035	-1.666100				.621648	2.100960
			.116941	-.139761					1.689988
Os ^{sc}	16	.520000	5.613073	.921955				.401894	-.084989
		.410578	2.785758	-6.692130	2.247034				1.669886
		.422395	-.590006	-3.018323	.000000				-.155759
			.870817	-.412886	-.139506				-2.473265
		.380252	.880133	-5.732892					-.122282
			.216440	-.103221		Tl	3	.630000	-1.235846
Ir	9	.641000	10.720016					.754005	1.875766
		.509960	2.445999	2.811037				.903742	1.759668
		.684971	.461792	1.304726					.168641
			-.565347	.859620				1.063512	.247614
		.471745	-4.545484	-1.635428					.022941
			.127199	-.151950		Tl ^{sc}	13	.550000	7.301886
Ir ^{sc}	17	.510000	4.904509	1.313786				.502423	3.326560
		.404469	3.243278	-7.315509	2.956978			.572016	1.272807
		.411426	-.380574	-3.504403	.000000				.012233
								.393185	-3.200652
									.186849
									-.170651
						Pb	4	.617500	.753143
								.705259	1.979927
								.846641	.864420
									.207711
								.971939	.374967
									.029256
						Bi	5	.605000	6.679437
								.678858	1.377634
								.798673	.655578
									-.513697
									-.402932
									.305314
								.934683	.378476
									-.023134

		.029217		
Po	6	.592500	10.411731	
		.647950	1.144203	-.735851
		.748947	.594562	-.353595
			.396354	-.031462
		.880468	.433232	
			.033886	
At	7	.580000	13.520411	
		.627827	.945557	-.965903
		.709823	.527078	-.318821
			.480774	-.034954
		.838365	.468948	
			.037544	
Rn	8	.570000	14.629185	
		.615182	.981832	-1.038963
		.676697	.612279	-.344122
			.549896	-.023760
		.788337	.557746	
			.045488	

TABLE II. Comparison of bond lengths of molecules calculated with our pseudopotentials (PSP) and obtained with GAUSSIAN 94 or NUMOL²¹ (AE) and the experimental data. All GAUSSIAN 94 calculations were done with a 6-311++G(3df,3pd) basis set if not otherwise mentioned. Bond lengths are given in Bohr.

Molecule	PSP	AE	Expt.	Ref.
H ₂	1.447	1.447	1.401	22
Li ₂	5.100 ^{sc} , 5.016	5.120	5.051	22
LiH	3.029 ^{sc} , 2.929	3.029	3.015	22
Be ₂	4.516 ^{sc} , 4.497	4.510	4.63	23
BF ₃	2.477	2.469	2.470	24
BH	2.363	2.371	2.373	22
CH ₄	2.072	2.072	2.052	25
C ₂ H ₂	r(CC) 2.263	2.270	2.274	24
	r(HC) 2.028	2.030	2.005	24
N ₂	2.067	2.070	2.074	22
NH ₃	1.932	1.932	1.912	24
HCN	r(CN) 2.169	2.174	2.179	26
	r(HC) 2.038	2.039	2.013	26
H ₂ O	1.836	1.834	1.809	24
CO	2.127	2.130	2.132	22
CO ₂	2.196	2.195	2.192	24
F ₂	2.622	2.613	2.668	22
HF	1.764	1.760	1.733	22
CH ₃ F	r(CF) 2.605	2.592	2.612	24
	r(HC) 2.082	2.082	2.069	24
Na ₂	5.76	5.64	5.818	22
NaH	3.534 ^{sc} , 3.381	3.529	3.566	22
Mg ₂	6.31	6.41	7.351	22
MgH	3.318 ^{sc} , 3.279	3.313	3.271	22
AlH	3.140	3.174	3.169	22
SiH ₄	2.808	2.820	2.795	27
SiO	2.827	2.861	2.853	22
SiF ₄	2.922	2.952	2.936	24
P ₂	3.547	3.542	3.578	22
PH ₃	2.696	2.704	2.671	28
PN	2.789	2.808	2.871	22
S ₃	3.595	3.609 ^a		
H ₂ S	2.553	2.558	2.524	24
CS	2.882	2.897	2.901	22
CS ₂	2.918	2.930	2.934	24
Cl ₂	3.725	3.742	3.756	22
HCl	2.436	2.440	2.409	22
CH ₃ Cl	r(CCl) 3.330	3.331	3.374	24
	r(CH) 2.072	2.072	2.060	24
K ₂	6.936	7.358 ^a	7.413	22
KH	2.200 ^{sc} , 2.969	2.303 ^a	2.307	22
CaH	3.706 ^{sc} , 3.187	4.126 ^a	3.783	22
ScH	3.304 ^{sc} , 3.182	3.300 ^b		
ScO	3.116 ^{sc}	3.109 ^b	3.152	22
TiO	3.018 ^{sc} , 2.840	3.020 ^b	3.062	22
VO	2.943 ^{sc} , 2.845	2.959 ^b	3.003	22
CrO	2.955 ^{sc} , 2.903	2.997 ^b	3.052	22
MnO	2.996 ^{sc} , 2.991	3.032 ^b	3.114	29
FeO	2.958	2.994 ^b	2.97	22
CoO	2.932	3.037 ^b	3.024	30
NiO	3.027	3.035 ^b		
NiH	2.726		2.787	22
CuO	3.153 ^{sc} , 2.749	3.176 ^b	3.258	22

CuH	2.731 ^{sc} , 2.463	2.755 ^b	2.765	22
Cu ₂	4.086 ^{sc} , 3.472	4.110 ^b	4.195	22
ZnO	3.157 ^{sc} , 2.886	3.161 ^b		
ZnH	3.010 ^{sc} , 2.858	3.025 ^b	3.013	22
GaH	3.176 ^{sc} , 3.095	3.173	3.143	22
GaO	3.167 ^{sc} , 3.022	3.173		
GaF	3.376 ^{sc} , 3.183	3.367	3.353	31
GeH ₄	2.861	2.896	2.882	24
GeO	3.010	3.074	3.118	22
As ₂	3.912	3.951	3.974	22
As ₄	4.551	4.573	4.602	24
AsH ₃	2.875	2.887	2.855	24
H ₂ Se	2.783	2.788	2.759	24
Se ₂	4.089	4.097	4.076	22
Se ₃ (C _{2v})	4.142	4.146		
SeO ₂	3.041	3.045	3.038	31
Br ₂	4.296	4.299	4.314	22
HBr	2.701	2.705	2.670	22
CH ₃ Br r(CH)	2.069	2.063	2.052	24
r(CBr)	3.636	3.635	3.653	24
BrF	3.326	3.322	3.318	22
BrF ₃ r ₁ (BrF)	3.437	3.434	3.420	24
r ₂ (BrF)	3.289	3.285	3.252	
Rb ₂	7.671 ^{sc} , 7.333		7.956	32
RbH	4.368 ^{sc} , 3.072		4.473	22
SrH	4.009 ^{sc} , 3.522		4.053	22
SrI ₂	5.560 ^{sc} , 5.327		5.69	24
SrO	3.591 ^{sc}		3.630	22
ZrO	3.235 ^{sc} , 2.848		3.234	22
RhC	3.027		3.049	22
PdH	2.865		2.889	
AgH	3.023 ^{sc} , 2.688		3.056	22
Ag ₂	4.717 ^{sc} , 3.760		4.67	22
CdH	3.323 ^{sc} , 3.108		3.329	22
InH	3.504 ^{sc} , 3.394	3.512 ^c	3.473	22
SnH	3.331		3.373	22
SnO	3.401		3.473	22
SnS	4.123		4.174	22
Sb ₂	4.624		4.70	33
SbCl ₃	4.414		4.411	34
Te ₂	4.824		4.832	22
H ₂ Te	3.146	3.156 ^c	3.133	24
HI	3.073	3.073 ^c	3.031	22
I ₂	5.029		5.039	22
Cs ₂	8.479 ^{sc} , 7.976		8.783	35
CsH	4.630 ^{sc} , 3.171		4.713	22
BaH	4.176 ^{sc} , 3.403		4.217	22
IrC	3.324		3.180	22
PtH	2.872		2.888	22
PtC	3.612		3.371	22
AuH	2.898 ^{sc} , 2.424		2.879	22
HgH	3.278 ^{sc} , 3.067		3.284	22
TlH	3.600 ^{sc} , 3.440		3.534	22
TlCl	4.472		4.81	22
PbH	3.433		3.475	22
PbS	4.237		4.526	22
PbCl ₂	4.552		4.609	34
BiH	3.374		3.411	22

^a: GAUSSIAN 94 with 3-21G basis set

^b: GAUSSIAN 94 with 6-311++G(3d,3pd) basis set

^c: calculated with NUMOL

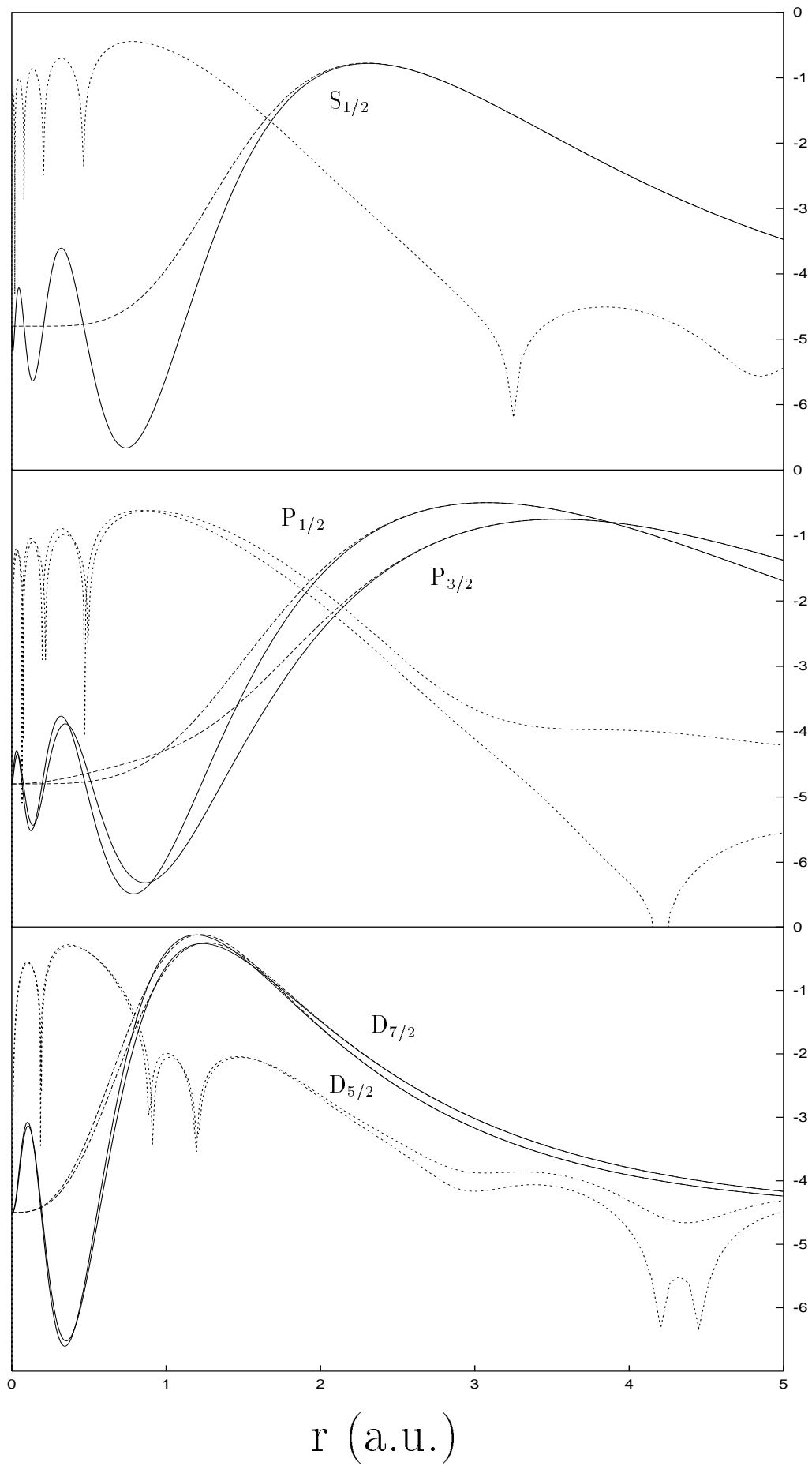
TABLE III. Transferability errors

Element	state	ΔE (Ha)	Error (Ha)
C	$2s^1 2p^3 3d^0$	0.3073	-0.40×10^{-3}
	$2s^2 2p^3 3d^0$	0.4294×10^{-1}	0.11×10^{-3}
	$2s^2 2p^1 3d^0$	0.3612	-0.44×10^{-3}
Si	$2s^2 2p^2 3d^1$	0.3882	0.95×10^{-4}
	$3s^1 3p^3 3d^0$	0.2529	-0.20×10^{-3}
	$3s^2 3p^3 3d^0$	-0.5293×10^{-2}	0.38×10^{-4}
Ge	$3s^2 3p^1 3d^0$	0.2673	-0.28×10^{-3}
	$3s^2 3p^2 3d^1$	0.2462	0.43×10^{-4}
	$4s^1 4p^3 4d^0$	0.2970	-0.48×10^{-3}
Sn	$4s^2 4p^3 4d^0$	-0.1682×10^{-1}	0.58×10^{-4}
	$4s^2 4p^1 4d^0$	0.2681	-0.23×10^{-3}
	$4s^2 4p^2 4d^1$	0.1879	0.52×10^{-4}
Pb	$5s^1 5p^3 5d^0$	0.2605	-0.40×10^{-3}
	$5s^2 5p^3 5d^0$	-0.2482×10^{-1}	0.46×10^{-4}
	$5s^2 5p^1 5d^0$	0.2510	-0.35×10^{-3}
Ti	$5s^2 5p^2 5d^1$	0.1084	0.34×10^{-4}
	$6s^1 6p^3 6d^0$	0.3181	-0.35×10^{-3}
	$6s^2 6p^3 6d^0$	-0.3587×10^{-1}	-0.41×10^{-5}
Ti ^{sc}	$6s^2 6p^1 6d^0$	0.2505	-0.46×10^{-3}
	$6s^2 6p^2 6d^1$	0.7216×10^{-1}	0.33×10^{-4}
	$4s^1 4p^1 3d^2$	0.1198	-0.17×10^{-3}
Ti ^{sc}	$4s^2 4p^0 3d^0$	0.1166×10^1	-0.47×10^{-1}
	$4s^0 4p^0 3d^0$	0.3258×10^1	-0.10
	$4s^2 4p^1 3d^2$	0.3593×10^{-1}	0.65×10^{-4}
Ti ^{sc}	$4s^1 4p^1 3d^2$	0.1198	-0.37×10^{-4}
	$4s^2 4p^0 3d^0$	0.1166×10^1	-0.31×10^{-2}
	$4s^0 4p^0 3d^0$	0.3258×10^1	-0.28×10^{-2}
Ti ^{sc}	$4s^2 4p^1 3d^2$	0.3593×10^{-1}	0.15×10^{-3}

FIG. 1. Relativistic all-electron (solid) and pseudo (dashed) wave functions of the valence electrons of gold. The difference between them is shown by the dotted line on a logarithmic scale.

Figure 1: Relativistic all-electron (solid) and pseudo (dash) wave functions for the valence states of gold. The difference between them is shown by the dotted line on a logarithmic scale.

$\psi(r) \cdot r$ (arbit. units)



Difference (arbit. units)

